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Advances in Asphaltene Petroleomics. Part 4. Compositional Trends of Solubility Subfractions Reveal that Polyfunctional Oxygen-Containing Compounds Drive Asphaltene Chemistry

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ABSTRACT: Asphaltenes have traditionally been conceived as highly aromatic, alkyl-deficient compounds enriched in pericondensed aromatic "island" motifs. This structural definition evolved into the general notion that aromatic core-dominated interactions (π -stacking) drive asphaltene aggregation, and heteroatom-based intermolecular forces have no significant effect on the overall solubility and aggregation behavior. However, the exclusion of heteroatoms in asphaltene chemistry is inconsistent with the Boduszynski continuum and known asphaltene properties, such as increased heteroatom content relative to maltenes, interfacial activity, and strong adsorption to polar stationary phases. Thus, to determine whether or not heteroatoms are involved in solubility, we have separated asphaltene fractions enriched in single-core (island) or multicore motifs (archipelago) according to their partitioning in n-heptane by two fractionation methods. In the first separation procedure, the acetone fraction from Wyoming deposit *n*-heptane asphaltenes (island-enriched) was adsorbed on polytetrafluoroethylene powder and Soxhlet extracted with *n*heptane. Subfractions were collected after one day, one week, one month, and three months of extraction, and the residue, *n*-heptane insoluble material, was recovered with a mixture of toluene and dichloromethane. In the second method, the acetone fraction from Athabasca bitumen *n*-heptane asphaltenes (archipelago-enriched) was fractionated by differential precipitation in mixtures of *n*heptane and toluene. The molecular composition of the asphaltene subfractions was accessed by positive-ion atmospheric pressure photoionization coupled to 9.4 T Fourier transform ion cyclotron resonance mass spectrometry and structures were determined by infrared multiphoton dissociation. The compositional trends for heteroatom content, double bond equivalents, and alkyl substitution suggest that the Boduszynski continuum can be extended to asphaltenes. In particular, the compositional range of polyoxygenated asphaltene compounds shifts toward lower aromaticity, whereas oxygen-depleted species are more aromatic. Moreover, the results demonstrate that polyoxygenated species (e.g., O_3 and S_2O_3 classes) are pivotal in asphaltene solubility, as they concentrate in the most polarizable and insoluble asphaltene subfractions. Therefore, the results support the existence of atypical asphaltene species with remarkably low aromaticity that reside in the most insoluble asphaltene subfractions because of their high heteroatom content. Such asphaltene compounds preferentially ionize as protonated molecules rather than radical cations and overlap the compositional range of interfacially active species, consistent with their tendency to participate in hydrogen bonding. Collectively, the results highlight the need for an asphaltene molecular model based on the existence of polyfunctional species capable of interacting with neighboring asphaltene molecules through several intermolecular forces, including London dispersion forces between aliphatic moieties, *π*-stacking of aromatic cores, hydrogen bonding between nitrogen and oxygen-containing functionalities, and acid/base interactions between carboxylic acids and pyridine rings.

INTRODUCTION

Classical View of Asphaltene Aggregation. For over five decades, asphaltene nanoaggregates have been described as clusters of aromatic cores surrounded by aliphatic moieties.¹ This view started in the 1960s with the work by Yen, who developed an X-ray diffraction method to study the structure of asphaltene aggregates.² The resulting Yen model is based on an oversimplification of the asphaltene molecular structure to capture what were thought, at the time, to be the key molecular interactions. Yen considered that asphaltenes were composed of large and fused aromatic cores combined with aliphatic moieties. Therefore, from his point of view, mixtures of graphite and polyethylene could simulate asphaltene structure and its X-ray diffraction properties.^{2,3} On that basis, Yen provided a hierarchical model for asphaltene aggregation in which the aromatic cores were the primary site for intermolecular interactions and the aggregate size progressed through π -stacking and subsequent clustering.³

To date, the main characteristics of the original Yen model are still the basis of asphaltene science: clusters of aromatic cores in which π -stacking is the major, *if not the only*, intermolecular force responsible for asphaltene aggregation.⁴⁻⁶

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It is believed that the dominant molecular motif consists of a single polycyclic aromatic hydrocarbon (HC) of ~7 fused rings, with an average molecular weight of ~750 g/mol, known as *island*.⁷⁻¹³ The aromatic cores are polarizable and exhibit induced dipole–dipole interactions that become stronger as a function of increasing aromatic core size.¹⁰ The influence of heteroatoms was largely limited to their effect within the aromatic cores, such as in pyridine and furan groups, where they promote charge separation, leading to dipole–dipole interactions. Therefore, it is generally accepted that the aggregation behavior of asphaltenes is exclusively driven by the aromatic cores, whereas the alkyl chains induce steric hindrance and limit the size of the aggregates.^{10,14,15}

Is π -Stacking the Dominant Intermolecular Interaction? Several reports highlight the use of molecular simulations to understand the intermolecular forces involved in asphaltene aggregation. These studies are controversial, in part, because the selected structures cannot accurately represent the complex molecular composition of petroleum asphaltenes. For instance, Ruiz-Morales et al.¹⁶ used molecular orbital calculations to investigate the effect of the structure, island (single-core) versus archipelago (multicore), on asphaltene dimerization and concluded that π -stacking was the pivotal interaction. However, the authors recognized that no heteroatom-containing molecules were employed for simplicity of the calculations. Other reports suggest that heteroatoms have little or no impact on the overall solubility and aggregation behavior of petroleum asphaltenes.¹⁵⁻¹⁷ For instance, Sedghi et al.¹⁵ determined the dimerization free energies for a set of heteroatom-containing island structures and concluded that π -stacking was the driving force for selfassembly. Recently, highly aromatic structures with O-, N-, and S-containing functionalities found in petroleum asphaltenes by atomic force microscopy¹⁸ were studied by quantum calculations.⁶ The results indicated that the aromatic cores were the primary site for interactions, regardless of the secondary effects of alkyl substitution and heteroatomcontaining functionalities.⁶ Other works contend that London forces dominate the solubility properties, and the molecular size and the active area for interaction dictate the degree of asphaltene self-association.^{17,19-21} For example, Rogel¹⁷ studied a set of eight island model structures by molecular mechanics and dynamics calculations and found that London dispersion forces have a leading role in the stability of asphaltene-resin aggregates, whereas hydrogen bonding had no significant impact on the interaction energy.¹

Theoretical studies on asphaltene aggregation are contradictory; several reports also suggest that hydrogen bonds enhance the stability of asphaltene aggregates and are as essential as π -stacking interactions.^{22–26} For instance, Tanaka et al.²³ performed molecular dynamics on proposed island and archipelago structures for Khafji asphaltenes. The authors found that several intermolecular interactions were responsible for the stability of the aggregates. At temperatures below 250 °C, hydrogen bonding had a significant role in the overall aggregate stability. However, the complete disruption of hydrogen bonds at temperatures higher than 350 °C led to aggregate stabilization by π -stacking. The authors also found that London forces between the aliphatic moieties were critical for the stability of the aggregates during heating. In another report, Müller et al.²⁴ pointed out the limitations imposed by the arbitrary choice of the molecular structures. The authors suggested that the molecules selected for molecular simulations

must contain carboxylic acids and pyridine rings, due to known asphaltene behavior after derivatization. It is well known that selective methylation of carboxylic acids and pyridine rings decreases the aggregation, which implies that hydrogen bonds and acid/base interactions are important in asphaltene self-assembly.²⁷ Other studies by quantum chemical calculations demonstrate that the number of aromatic rings is not the only crucial factor in the stability of asphaltene dimers.^{25,28} For example, Wang et al.²⁵ concluded that the presence of heteroatoms in both alkyl-side chains and aromatic cores strengthens the stability of asphaltene aggregates via hydrogen bonding.

Heteroatoms and Petroleum Chemistry. The exclusion of heteroatoms in asphaltene solubility and aggregation properties not only ignores the rules that govern the continuum composition of petroleum discovered by Boduszynski 30 years ago²⁹ but also discounts the importance of the widely documented increase of heteroatom concentrations in the vacuum bottoms and asphaltenes. The Boduszynski continuum dictates that for a given homologous series of petroleum compounds (e.g., linear alkanes and $C_n H_{2n+2}$), the boiling point increases as a function of increasing molecular weight. All of the homologous series exhibit the same trend. Further, at a given carbon number, the series with the highest number of aromatic rings and heteroatomic functionalities has the highest boiling point.³⁰ Therefore, within a distillation cut, aromatic species with high heteroatom content must have a lower carbon number and vice versa.³¹ McKenna et al.³² demonstrated these rules for Athabasca bitumen distillation cuts. The authors concluded that for the fixed range of carbon number ~20-35, HCs (species composed of C and H) boiled between 343 and 375 $^\circ \text{C}.$ The increase in heteroatom content by one and two sulfur atoms shifted the boiling ranges to 375-400 and 400-425 °C. Finally, a higher dipole moment induced by oxygen (species composed of C, H, one S atom, and one O atom) increased the boiling point to 425-450 °C.³² The authors concluded that for every added heteroatom, the carbon number must decrease by 2-3 carbon atoms to reside in the same boiling cut. Most importantly, a central feature of the Boduszynski continuum is the role of heteroatoms in petroleum distillation trends (highlighted above) that resulted in a \sim 80 °C shift in the boiling point with the addition of only a single sulfur and oxygen atom. Thus, Boduszynski suggested that distillation residues exhibit a high boiling point because of stronger intermolecular interactions between abundant polyaromatic structures and heteroatomic functionalities that promote hydrogen bonding and acid/base interactions.^{33,34} The conclusion relied heavily on the data that asphaltenes were not high-molecular weight species (~less than 2000 Da) and when combined with the quantitative bulk elemental data, suggested that "the observed changes in heteroatom concentration and molecular weight with increasing atmospheric equivalent boiling point (AEBP) imply a high concentration of compounds having several heteroatoms per molecule."29

Extraordinarily, the Boduszynski continuum predicted the low-molecular weight nature of petroleum asphaltenes.^{33,35,36} Thirty years ago, Boduszynski suggested that asphaltenes must occupy a compositional range with a carbon number similar to distillable maltenes, but higher double bond equivalents (DBE = number of rings + double bonds to carbon) and abundant heteroatom-containing functionalities. Moreover, Boduszynski hypothesized that all nonaggregated petroleum compounds are *n*-heptane soluble, and only aggregated species exhibit insolubility. Therefore, if the Boduszynski continuum is correct, the solubility/aggregation behavior of petroleum asphaltenes must be the result of the synergy between several intermolecular forces, including π -stacking, hydrogen bonding, acid/base interactions between carboxylic acids and nitrogen bases, and London forces between aliphatic moieties, as pointed out by Yarranton, Gray, Silva, Acevedo, and Murgich et al.^{22,37–42} Eventually, comprehensive and selective fractionation of distillation residues and asphaltenes should yield fractions enriched in species with a *distillable* nature and higher solubility in *n*-heptane.^{33,34,43} Simply, if the increased boiling point of asphaltenes is due, in part, to intermolecular interactions, removal of these interactions (albeit difficult) should yield species of a lower apparent boiling point.

Separations Are Necessary to Access Asphaltene Chemistry. Contrary to theoretical studies, separation of petroleum asphaltenes into solubility cuts with different contents of V, Ni, O, and N, suggests a link between heteroatom-containing compounds and stronger self-association. For example, Wattana et al.44 fractionated asphaltenes from crude oils and deposit samples by differential precipitation in mixtures of dichloromethane/n-pentane (DCM/nC_5) . In that method, asphaltenes are dispersed in a "good" solvent such as DCM and sequentially precipitated by the stepwise addition of a "poor" solvent such as n-pentane. Therefore, the fraction precipitated with the least amount of nC_5 comprises the most unstable (and therefore most polarizable) compounds. Wattana and co-workers found that asphaltenes from challenging oils, with known deposition issues in production, were enriched in the most polarizable fraction compared with asphaltenes from stable crude oils.⁴ The authors determined that the most unstable/polarizable fractions, from geologically diverse petroleum samples, exhibited disproportionate aggregation trends and a much higher apparent dipole moment. Similarly, Trejo, Spiecker, and Gawrys et al.^{45–48} found that unstable asphaltene fractions had lower H/C ratios, higher oxygen and nitrogen content, and decreased solubility in toluene, compared with sulfur-enriched stable asphaltene fractions. The authors suggested that unfractionated asphaltenes in the solution present a cooperative stabilization, in which stable species disrupt strong intermolecular forces, such as hydrogen bonding, that drive stronger intermolecular interactions in the less soluble fractions.

Although differential precipitation is an attractive method to separate unstable/polarizable asphaltene species from "nonproblematic" compounds, the fractionation method suffers limitations that arise from the high concentration of asphaltenes in the initial solution in the good solvent (e.g., DCM or toluene). Thus, the separation starts with a mixture of molecular species ("monomers") and aggregates ("polymers"). Therefore, precipitation via the stepwise addition of a poor solvent (e.g., *n*-pentane or *n*-heptane) is due to contributions from both molecular solubility (intermolecular interactions) and aggregate colloidal stability (interactions between molecular aggregates). We hypothesize that the sonication of the initial asphaltene solution and the precipitating mixture could help to decrease asphaltene aggregation, enhancing the separation by solubility.

Differential precipitation by use of acetone as poor solvent yields asphaltene fractions with remarkable differences in apparent molecular weight, polydispersity, aggregation trends, heteroatom content, and molecular structure. For instance, Buenrostro-Gonzalez et al.,⁴⁹ fractionated asphaltenes in mixtures of toluene/acetone and reported results that contradict the modified Yen model.^{1,10} The authors found that the fraction with the highest solubility in the poor solvent (acetone) exhibited increased aromaticity, fewer alkyl chains, and the highest concentration of vanadyl porphyrins.⁴⁹

Other authors have approached asphaltene fractionation via Soxhlet extraction/extrography, which depending on the conditions (e.g., whether a stationary phase is used or not, particle size of the solid to be extracted), may enable a separation by "molecular selectivity". For instance, Strausz et al.³⁰⁻⁵² fractionated bitumen asphaltenes by Soxhlet extraction with acetone. The authors found that asphaltene fractions soluble in acetone presented weaker aggregation tendencies, lower apparent molecular weight, higher aromaticity, and enrichment in vanadium.

Recently, Chacón-Patiño et al.^{53,54} developed an extrography separation with silica gel that yields asphaltene fractions enriched in island or archipelago motifs. The fractionation employs two solvent series. The first series consists of acetone and acetonitrile (ACN); the second series is a polarity gradient composed of *n*-heptane (nC_7) , toluene (Tol), tetrahydrofuran (THF), and methanol (MeOH). The authors demonstrated that the initial extraction with acetone enables selective separation of highly aromatic, single-core compounds. Acetone assists the separation of island species because the dominant intermolecular forces consist of dipole-dipole interactions. The later extraction with mixtures of Tol/THF and THF/ MeOH, with solvent strengths similar to acetone, but with predominant hydrogen-bond donor-acceptor interactions, yield fractions enriched in N- and O-containing multicore structures (archipelago motifs) that exhibit stronger selfassociation in Hep/Tol than the acetone fractions.^{53,54} The stronger aggregation of archipelago-enriched fractions (e.g., Tol/THF fraction) is one of the reasons for the incomplete characterization of asphaltenes by mass spectrometry. For more than a decade, the dominance of island structures in petroleum asphaltenes received strong support from the mass spectrometry community.⁵⁵⁻⁵⁸ Research groups focused on the characterization of whole/unfractionated asphaltene samples, in which ionization is limited to the island species because of the heterogeneous aggregation of petroleum asphaltenes. Recent reports demonstrate that a more comprehensive mass spectrometry characterization of asphaltenes, as well as other petroleum fractions such as naphthenic acids and basic nitrogen-containing compounds, is possible by sample fractionation before mass spectrometry (MS) analyses.^{53,59–63}

The present work focuses on understanding the compositional trends of asphaltene subfractions as a function of partitioning in *n*-heptane. Asphaltene extrography fractions enriched in island or archipelago motifs were separated by exhaustive Soxhlet extraction and differential precipitation. Specifically, the acetone fraction from the Wyoming deposit nC_7 asphaltenes (island-enriched) was adsorbed on polytetrafluoroethylene (PTFE) powder and separated into solubility subfractions by extended Soxhlet extraction with *n*-heptane. The acetone fraction from Athabasca bitumen nC_7 asphaltenes (archipelago-enriched) was fractionated by differential precipitation in Hep/Tol. The molecular-level characterization of the solubility subfractions was performed by positive-ion atmospheric pressure photoionization (+APPI) coupled to 9.4 T

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Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and infrared multiphoton dissociation (IRMPD). The results reveal trends in the heteroatom content, alkyl substitution, aromaticity, and structure that agree with the Boduszynski continuum and highlight the existence of polyfunctional, nearly saturated species that are pivotal in the self-assembly and solubility behavior of petroleum asphaltenes. The results also demonstrate that the low-DBE molecules overlap the compositional range of interfacially active asphaltene compounds. Such low-DBE species reside in the most insoluble asphaltene subfractions, likely because of their ability to hydrogen bond with several neighboring molecules.

EXPERIMENTAL SECTION

Materials. High-performance liquid chromatography-grade *n*-heptane (nC_7 or Hep) DCM, toluene (Tol), acetone, ACN, water, and methanol (MeOH) were obtained from J.T. Baker (Phillipsburg, NJ) and used as received. THF with no solvent stabilizer was purchased from Alfa Aesar (Ward Hill, MA). Whatman filter paper grade 42 was used for asphaltene isolation from crude oils. High-purity glass microfiber thimbles were utilized for asphaltene cleaning and fractionation by Soxhlet extraction (Whatman, GE Healthcare, Little Chalfont, U.K.). Chromatographic-grade silica gel (100–200 mesh, type 60 Å, Fisher Scientific) was used for extrography. Polytetrafluoroethylene (PTFE or Teflon) powder (particle size = 1 μ m, Sigma-Aldrich, St. Louis—Missouri) assisted asphaltene fractionation by extended Soxhlet extraction. Wyoming deposit and Athabasca bitumen samples were supplied by Nalco Champion and CanmetENERGY.

Asphaltene Precipitation from Crude Oils and Extrography Separation. nC_7 asphaltenes were isolated from crude oils through a method reported elsewhere.⁶⁴ Briefly, the dropwise addition of *n*heptane (400 mL) to the crude oil (10 mL) was performed under sonication (Branson Ultrasonics, Danbury, CT, 22 kHz, and 130 W) and refluxed heating (~85 °C). The mixture was allowed to stand for 12 h. Subsequently, asphaltenes were collected by filtration, placed in a Soxhlet apparatus, and extracted with *n*-heptane for 72 h. The Soxhlet apparatus was set to complete an extraction cycle every ~5 min, and the temperature in the thimble reservoir was ~50 °C. Asphaltenes were recovered by dissolution in hot toluene (~70 °C). Sample cleaning was carried out by four cycles of asphaltene crushing and Soxhlet extraction with *n*-heptane. The cleaning process decreases the amount of co-precipitated/occluded maltenes.

Athabasca bitumen and Wyoming deposit nC_7 asphaltenes were separated into fractions enriched in island or archipelago motifs following the method reported by Chacón-Patiño et al.⁵³ In short, asphaltenes were dissolved in DCM (50 μ g/mL) and adsorbed on silica gel under a N₂ atmosphere. The dry solid mixture of silica gel and asphaltenes was placed in a Soxhlet apparatus and sequentially extracted with two solvent series. The first series consists of acetone and ACN; the second series comprises Hep, Hep/Tol (1:1), Tol, Tol/THF (1:1), THF, and THF/MeOH (9:1). Mass loading below 1% (<10 mg of asphaltenes per gram of silica gel) and drying the silica gel after the first solvent series are critical conditions for the success of the separation.

Asphaltene Separation on PTFE Powder. Acetone extrography fraction (30 mg) from Wyoming deposit nC_7 asphaltenes (labeled as Wyoming acetone fraction) was dissolved in toluene (50 ppm) and mixed with the PTFE powder (6 g). Mixture was stirred overnight under N₂. Subsequently, the dry mixture (PTFE powder/asphaltenes) was placed in a Soxhlet apparatus and extracted with *n*-heptane. Extractions were carried out under N₂ to prevent asphaltene oxidation. Subfractions were collected after one day, one week, one month, and three months of nC_7 extraction. Finally, a residue was collected after 2 h of extraction with 1:1 Tol/DCM. The PTFE subfractions were labeled as one-day, one-week, one-month, threemonths, and residue.

Separation by Differential Precipitation. Acetone fraction (30 mg) from Athabasca bitumen nC_7 asphaltenes (labeled as Athabasca bitumen acetone fraction) was dissolved in 8 mL of toluene. The asphaltene solution was sequentially titrated with *n*-heptane, added dropwise under sonication (Branson Ultrasonics, Danbury, CT, 22 kHz, and 130 W). The contact time between the asphaltene solution and the precipitant was 4 h. The most unstable/polarizable asphaltene subfraction was precipitated with the lowest volume of *n*-heptane (40%) and recovered by centrifugation (Eppendorf 5804 R) at 5000 rpm for 20 min. Afterward, the remnant solution was mixed with additional *n*-heptane until reaching 60% *n*-heptane by volume. The destabilized asphaltenes were recovered by centrifugation, and the supernatant was combined again with n-heptane. The precipitation process was carried out four times, with 40, 60, 80, and 95% of nheptane. The precipitated subfractions were labeled as PPT/40, PPT/ 60, PPT/80, and PPT/95. The most soluble asphaltenes comprise the fraction that remains in solution after 95% of *n*-heptane addition; that fraction was labeled as Soluble/95.

Isolation of the Interfacial Material from Wyoming Acetone Fraction by Wet Silica Method. Water-saturated silica gel was prepared as reported by Jarvis et al.⁶⁷ Wyoming acetone fraction (5 mg) was dissolved in toluene (250 ppm) and mixed with wet silica (0.5% mass loading). The slurry was placed in a glass column and washed with toluene to extract noninterfacially active asphaltenes. The interfacial material was eluted with Tol/THF/MeOH (2/2/1).

Positive-Ion Atmospheric Pressure Photoionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry [(+) APPI FT-ICR MS] and IRMPD. Asphaltene samples were dissolved in toluene at a concentration of 50 $\mu g/mL$ and directly infused into a Thermo Fisher Ion Max APPI source (Thermo Fisher Scientific, Inc., San Jose, CA, U.S.). The vaporizer temperature was set at 320 °C, N₂ sheath gas was operated at 50 psi, and N2 auxiliary gas was employed at 32 mL/min. Gas-phase neutrals were photoionized by a 10 eV Krypton lamp. Molecular characterization was carried out with a custom-built 9.4 T Fourier transform ion cyclotron resonance mass spectrometer.⁶⁸ Data collection was performed by a modular ICR data acquisition system (PREDATOR).⁶⁹ Selective isolation of high-DBE precursor ions for tandem-MS was carried out by stored waveform inverse Fourier transform excitation.⁷⁰ The conditions for MS and IRMPD/MS analyses are reported by Niles et al.⁷¹ and in the first part of the series Advances in Asphaltene Petroleomics.⁶⁵ Molecular formula assignment and data visualization by isoabundance colorcontoured plots of DBEs versus carbon number were performed with PetroOrg N-18.3 Software.7

RESULTS AND DISCUSSION

For over five decades, the petroleum community has described asphaltenes as highly aromatic alkyl-deficient island motifs.^{4,13} It is well documented that Wyoming deposit asphaltenes exhibit abundant highly aromatic/alkyl-deficient compounds whose behavior in thermal cracking and tandem-MS suggests a high concentration of single-core/island motifs.^{54,73} Therefore, to acknowledge the classical asphaltene literature, we begin by focusing on the compositional tendencies of the Wyoming acetone fraction (island-enriched) as a function of partitioning in *n*-heptane.

Figure 1, upper panel, illustrates the separation of the Wyoming acetone fraction by adsorption on PTFE powder and subsequent extraction with *n*-heptane. Asphaltene adsorption onto a nonpolar stationary phase such as PTFE increases the solvent-accessible surface area, enhancing the fractionation by extractability. It is important to note that the extraction process was carried out under N_2 to decrease possible asphaltene oxidation. Figure 1, lower panel, presents the gravimetric yields for the separation (gray bars) and the monomer ion yield (MIY) or ionization efficiency in positive-ion APPI (red bars). Regardless of the solubility definition of asphaltenes, more



Figure 1. Upper panel: Fractionation of the Wyoming acetone fraction by extended Soxhlet extraction with nC_7 . Lower panel: gravimetric yield for the fractionation process (gray) and ionization efficiency, or MIY (MIY, red, s^{-1}), for positive-ion APPI MS analyses. The results suggest a direct correlation between ionization efficiency in APPI and asphaltene partitioning (or solubility) in nC_7 .

than 80% of the sample was recovered with *n*-heptane after one week of extraction; after three months, more than 95% was collected. In the end, only $\sim 1-2\%$ of the sample was extracted with a stronger solvent mixture (Tol/DCM). It is important to note that the acetone fractions from several asphaltene samples (e.g., Wyoming deposit, Athabasca bitumen, Arabian Heavy, and South American medium) exhibit much weaker aggregation tendencies in Hep/Tol than unfractionated asphaltenes and the rest of the extrography fractions (e.g., Tol/THF and THF/MeOH).^{53,54} Therefore, the high nC_7 extractability of the Wyoming acetone fraction was, to some extent, anticipated. Also, it is critical to point out that the same fractionation procedure was applied to the Tol/THF extrography fraction (archipelago-enriched) from Wyoming deposit nC_7 asphaltenes. The amount of material recovered after three months was so low that it was insufficient for mass spectrometry characterization.

With regard to the production efficiency of nonaggregated asphaltene ions by APPI, MIY is defined as a value inversely proportional to the accumulation period required to detect a target signal magnitude at a given sample concentration.⁶⁵ Thus, MIY reflects ionization efficiency as measured by MS analysis. The ionization behavior of the PTFE subfractions agrees with our previous reports because it suggests an inverse correlation between fraction insolubility in *n*-heptane, and ion production by APPI.^{53,54} Specifically, the MIY of the whole Wyoming acetone fraction (MIY = \sim 44) is similar to that of the one-day subfraction (MIY = \sim 54). The later-extracted species are more challenging to ionize; one-week, one-month, three-months, and residue subfractions present a \sim 3-, \sim 10-, ~16-, and ~30-fold decrease in MIY compared with the oneday subfraction. Efficient ionization of the whole Wyoming acetone fraction is consistent with the high concentration of the one-day subfraction (~ 63 wt %) and the possible cooperative stabilization between stable and unstable asphaltene species, as previously reported by Trejo, Spiecker, and Gawrys et al.45**Molecular Characterization.** Broadband FT-ICR MS is uniquely suited for molecular-level characterization of ultracomplex mixtures because it can resolve and identify tens of thousands of elemental compositions in a single analysis in a matter of minutes, irrespective of the boiling point.^{74–79} When combined with separations, FT-ICR MS constitutes a powerful tool to assess petroleum molecular composition and understand the compositional trends responsible for petroleum phase behavior, fouling, and refining.^{75,80–88}

Molecular formulas were assigned to the mass spectral peaks and sorted by heteroatom groups (e.g., S_x , O_x , and N_xO_y), heteroatom classes (e.g., S_1 , S_2 , O_1 , and N_1O_1), DBEs (DBE = sum of rings plus double bonds), and carbon number. Figure 2



Figure 2. Heteroatom group distribution for the PTFE subfractions from the Wyoming acetone fraction. The results suggest that HCs, sulfur (S_x) , and nitrogen-containing species (N_x) do not drive asphaltene insolubility in nC_7 . The most soluble subfraction, one-day, is represented by orange bars, whereas the most insoluble subfraction, the residue, is represented by green bars.

presents the heteroatom group distribution for the PTFE subfractions derived from the Wyoming acetone fraction. The results suggest that HCs, sulfur, and nitrogen-containing compounds (groups HC, S_{xv} , N_{xy} and N_xS_y) do not drive asphaltene insolubility in nC_7 because the relative abundances of these heteroatom groups gradually decrease as a function of the extraction time. In particular, the residue (green bars) contains HC, S_{xy} and N_x groups with a relative abundance ~12-, ~6-, and ~5-fold lower than the one-day subfraction (orange bars).

Conversely, oxygen-containing groups (i.e., $O_{xy} N_x O_{yy}$ and $N_x O_y S_z$) increase in relative abundance as the extraction proceeds. For instance, the residue is enriched in the groups O_x (~30%) and $N_x O_y$ (~24%), compared with the one-day subfraction ($O_x = \sim 21\%$ and $N_x O_y = \sim 10\%$). Therefore, the results suggest that heteroatom-based intermolecular forces (e.g., hydrogen bonding) are pivotal in asphaltene solubility. Similarly, the relative abundance of the $O_x S_y$ group increases from day number one (~30%) until a month of extraction (36%), suggesting that polarizable S-containing groups, such as sulfoxides, are also critical in asphaltene assembly.^{89–91} These trends agree with the report by Trejo et al.,⁴⁵ who fractionated Maya and Isthmus asphaltenes based on partition in Hep/Tol. The authors found that the subfractions with poor solubility exhibited higher bulk oxygen content. In another study, Qiao et al.⁹⁰ demonstrated stronger aggregation trends for asphaltene samples enriched in sulfoxides.

To facilitate interpretation of the compositional trends, assigned formulas were sorted by heteroatom content (e.g., species composed of carbon, hydrogen, and one oxygen atom define the class O_1) and presented as three-dimensional plots of DBE (y-axis) versus carbon number (x-axis), with the



Figure 3. Isoabundance color-contoured plots of DBEs (DBE = number of rings plus double bonds to carbon) vs carbon number for HCs (HC group) for the Wyoming acetone PTFE subfractions. Radical cations ($M^{+\bullet}$) and protonated molecules ($[M + H]^+$) are plotted together. The results suggest that aromaticity (high DBE/low H/C) is the driving factor in the insolubility of HCs in nC_7 .

relative abundance represented by a color scale. Therefore, in the DBE versus carbon number plot for a particular heteroatom class, compounds that belong to the same homologous series have equal DBE (rings and double bonds), but different carbon numbers (CH₂ units). Figure 3 presents the isoabundance color-contoured plots of DBE versus carbon number for the HCs (group HC) of the Wyoming acetone PTFE subfractions. It is essential to keep in mind that atmospheric pressure photoionization produces radical cations $(M^{+\bullet})$ and protonated molecules $([M + H]^{+})^{.92}$ In Figure 3, both types of cations are plotted together. The progression of the compositional range suggests that hydrogen deficiency (low H/C ratios and high DBE values) drives the low-extraction efficiency of HCs in *n*-heptane. In particular, the compositional range for HC species for the one-day subfraction exhibits more alkyl substitution (more extended homologous series), a higher abundance-weighted H/C ratio (~ 0.81) , and a lower abundance-weighted DBE (~ 26.7) , than the subfraction extracted after three months (H/C \approx 0.64, DBE \approx 30.1) and the residue (H/C \approx 0.60, DBE \approx 29.0). Therefore, the behavior of HCs (no heteroatoms) supports correlations between the composition and solubility implied by the modified Yen model: aromatic core size (higher DBE) and hydrogen deficiency (lower H/C ratios, shorter homologous series) increase with decreasing *n*-heptane extractability.

Compositional Trends for Heteroatom-Containing Asphaltene Compounds. Figure 4 presents the compositional trends within O-containing groups. Upper and lower panels show the compound class distribution for the groups O_x (classes O_1 , O_2 , O_3 , O_4 , and O_5) and N_1O_{ν} (N_1O_1 , $N_1O_{2\nu}$ N_1O_{31} N_1O_{41} and N_1O_{5}). The trends demonstrate the central role of polyoxygenated species in the solubility behavior of petroleum asphaltenes. The monofunctional O1 class (compounds that contain only one oxygen atom) decreases in relative abundance as a function of the extraction time. The one- day subfraction contains $\sim 13\%$ of O₁ species, whereas the residue contains ~7%. On the other hand, polyoxygenated compounds steadily increase in relative abundance during the extraction process. The three months and residue subfractions are enriched in polyoxygenated classes O2, O3, O4, and O5. Specifically, the relative abundance of the O_2 class for the residue is \sim 2-fold higher than the one-day subfraction. The O₂ class could correspond to a carboxylic acid group, two alcohols, two furan rings, or a combination of the two latter functionalities. The increase in relative abundance is more prominent for higher-order oxygen-containing classes. The residue reveals O3 and O4 species (polyfunctional) with ~4and ~15-fold higher relative abundance than the one-day subfraction. The N_1O_{ν} species present similar trends. The



Figure 4. Compositional trends for O-containing classes for the Wyoming acetone PTFE subfractions. Note that the poly-oxygenated species (classes O_{2-5}) increase in relative abundance during the extraction process.

three months and residue subfractions are enriched in N_1O_2 , N_1O_3 , and N_1O_4 species.

The compositional trends in Figure 4 indicate that polyfunctional species play a central role in asphaltene intermolecular forces that promote stronger intermolecular interactions between asphaltene species, thus low-extraction efficiency in n-heptane. The results point out the need for an asphaltene aggregation model that involves heteroatomcontaining functionalities and multiple intermolecular forces between monofunctional and polyfunctional species. In this regard, the data presented herein are in complete agreement with Agrawala and Yarranton, who concluded that polyfunctional compounds are critical in asphaltene intermolecular interactions.³⁷ They proposed that petroleum is a mixture of monofunctional and polyfunctional species, whose intermolecular interactions, thus aggregation, could be described by a model analogous to linear polymerization.³⁷ The authors suggested that asphaltenes are enriched in polyfunctional compounds, whereas maltenes are enriched in monofunctional species. In a polymerization-like reaction, polyfunctional compounds act as propagators; in an asphaltene self-assembly, those compounds promote stronger aggregation because they



Figure 5. Isoabundance color-contoured plots of DBE vs carbon number for the O_{1-5} classes for the Wyoming acetone PTFE subfractions. Radical cations ($M^{+\bullet}$) and protonated molecules ($[M + H]^+$) are plotted together. Higher-order oxygenated species with poor solubility exhibit lower DBE values, suggesting the presence of strong intermolecular forces (e.g., hydrogen bonding) responsible for low partitioning in nC_7 .

establish multiple intermolecular bonds with two or more neighboring molecules. On the other hand, monofunctional species can be considered as terminators because they hinder asphaltene aggregation because of their inability to bond with more than one neighbor.³⁷ Along similar lines, Gray et al.⁴⁰ suggested that asphaltene molecules are composed of multiple active sites such as aromatic cores, saturated moieties, pyridine rings, phenol groups, and carboxylic acids. Those molecular motifs are equally important for asphaltene aggregation. The authors suggested that polyfunctional asphaltene species are consistent with an aggregation model in which several cooperative interactions support the existence of supramolecular networks. However, the strict definition of propagators and terminators based solely on chemical functionality (functionalities) and/or structural motifs is difficult because the influence of either can be affected by steric hindrance.

Extending the Boduszynski Continuum to "Nondistillable" Petroleum Fractions. Figure 5 presents the isoabundance color-contoured plots of DBE versus carbon number for O_x species for the PTFE subfractions. Radical cations (M^{+•}) and protonated molecules ([M + H]⁺) are plotted together. In general, the progression of the compositional range suggests that higher-order oxygen-containing species, with low partitioning in *n*-heptane (class O_5 , residue subfraction), exhibits lower DBE values (abundance-weighted DBE \approx 19.8) than more soluble/mono-oxygenated compounds (oneday subfraction, class O₁, abundance-weighted DBE \approx 24.8). Although asphaltenes are acknowledged as "nondistillable" species, and thus cannot be considered as a distillate cut, the results are consistent with the rules of the Boduszynski continuum, and suggest that subfractions with low partitioning in *n*-heptane are enriched in polyoxygenated compounds likely capable of hydrogen bonding. Therefore, a higher oxygen content (higher probability of hydrogen bonding interactions) offsets a lower aromaticity.^{29,32,93,94} Admittedly, the trend is not as dramatic as those previously documented in distillates,³² but the change in DBE is accompanied by a similar shift in H/C and is thus worth noting.

The trends in Figure 5 highlight that both oxygen content (hydrogen bonding) and aromaticity (π -stacking) contribute to the solubility behavior of asphaltenes. Within the same PTFE subfraction (columns), the number of rings and double bonds (DBE) decrease as a function of increasing the number of oxygen atoms. Thus, higher oxygen content offsets a lower DBE, suggesting that low-DBE asphaltene species reside in the most insoluble subfraction because of their high heteroatom content. Within the same class (rows), the increase in DBE, from one-day to one-month (e.g., class O₁, abundance-weighted DBE from ~24.8 to ~27.0), suggests that the relevant role of π -stacking in the solubility behavior of more

than 90 wt % of the sample. That result is consistent with the molecular composition of the acetone fraction from Wyoming deposit nC_7 asphaltenes, a sample enriched in alkyl-deficient/ high-DBE island compounds.⁵⁴

Figures S1 and S2 of the Supporting Information present the isoabundance color-contoured plots of DBE versus carbon number for S_x and N_x species for the Wyoming PTFE subfractions [radical cations ($M^{+\bullet}$) and protonated molecules are plotted together]. The results demonstrate the lack of clear trends between the composition of S_x (x = 1-3) and N_x (x = 1-2) species and nC_7 insolubility. Simply, an increase in the heteroatom content does not correlate with decreased solubility. However, the incorporation of oxygen (Figure S3, N_1O_x species) reveals compositional tendencies consistent with those presented in Figure 5 (for the O_x species), as increased oxygen content results in decreased solubility.

Compositional Trends for O_xS_y **Species.** Figure 6 presents the class distributions for O_xS_1 and O_xS_2 species for



Figure 6. Compositional trends for $O_x S_y$ species for the Wyoming acetone PTFE subfractions. The results demonstrate that the residue (green bars) is enriched in higher-order oxygen-containing sulfur compounds.

the PTFE subfractions derived from the Wyoming acetone fraction. The results demonstrate that the one-day subfraction contains more mono-oxygenated classes O_1S_1 and O_1S_2 , with a ~3- and ~2-fold higher relative abundance than the residue. On the other hand, the insoluble subfractions reveal abundant polyoxygenated species. In particular, three-months and residue contain O_3S_1 species with a ~3- and ~4-fold higher relative abundance than the one-day subfraction. Note that O_xS_y species dominate the composition of the petroleum interfacial material, which has been shown to be asphaltenic.^{67,95} Thus, because a fraction of asphaltenes exhibit interfacial activity at the oil/water interface, the molecular composition of O_xS_y classes is discussed in detail below.

Figure 7 presents isoabundance color-contoured plots of DBE versus carbon number for the O_1S_2 , O_2S_2 , and O_3S_2 classes for the PTFE subfractions. Again, radical cations (M^{+•}) and protonated molecules ([M + H]⁺) are plotted together. The results suggest that most of the mono-oxygenated species (O_1S_2 class) occupy a compositional range at a DBE value higher than 18 (likely a six-ring fused aromatic core) and short homologous series (~10–15 members). However, it is important to note that the compositional range for the O_1S_2 class for the three-months and residue subfractions exhibit a bimodal DBE distribution with low-DBE (<10) species of low relative abundance. Indeed, the most insoluble subfraction contains the lowest abundance-weighted DBE and the highest abundance-weighted H/C ratio of the extraction periods (Figure 7, top row).

The bimodal DBE distributions for species with low/high DBE values are more prominent for higher-order oxygencontaining classes. The O_2S_2 and O_3S_2 classes exhibit more abundance of low-DBE species as the extraction proceeds. Moreover, the O_3S_2 class, detectable only after one month of extraction, exhibits a well-defined gap between the high- and the low-DBE distributions. We hypothesize that heteroatoms in high-DBE species are embedded within aromatic cores, for example, thiophene and furan rings, consistent with the



Figure 7. Isoabundance color-contoured plots of DBE vs carbon number for O_xS_2 species for the Wyoming acetone PTFE subfractions. $M^{+\bullet}$ and $[M + H]^+$ cations are plotted together. The results demonstrate that the compositional range of higher-order O-containing classes shifts toward lower DBE values. This effect is more evident for the residue subfraction and suggests that π -stacking is not the only intermolecular force that governs asphaltene solubility.



Figure 8. Upper panel: Separate isoabundance color-contoured plots of DBE vs carbon number for radical cations M^{+*} and protonated molecules $[M + H]^+$ for the O_2S_2 class for the Wyoming acetone PTFE subfractions. Lower panel: abundance-weighted H/C ratios, and ratio of the relative abundance of protonated molecules to radical cations ($[M + H]^+/M^{+*}$) for the O_2S_2 class. The results suggest that the residue is enriched in low-DBE species that preferentially produce protonated species from atmospheric pressure photoionization.

modified Yen model view of the "aromatic driven" asphaltene composition. However, the low-DBE compounds must contain more polarizable functionalities, such as thiols, carboxylic acids, and sulfoxides, capable of stronger intermolecular forces. Therefore, it is likely that low-DBE compounds reside in the asphaltene subfraction with the lowest extraction efficiency in n-heptane because of chemical functionality and not aromaticity.

The compositional trends for the $O_x S_y$ species support the notion that the Boduszynski continuum extends to "nondistillable" petroleum fractions. Nonextractable species with highoxygen content (residue, class O_3S_2) exhibit the lowest abundance-weighted DBE and the highest abundanceweighted H/C ratio, indicating that lower aromaticity is offset by higher oxygen content, which is likely present in functionalities capable of hydrogen bonding (or acid/base interactions). Evidence of the suspected trend can be gleaned from ionization trends (ion type) in APPI. Representation of radical cations $(M^{+\bullet})$ and protonated molecules generated by APPI into separate DBE versus the carbon number plots provides additional insights.⁹⁶ Figure 8, upper panel, shows separate isoabundance color-contoured plots of DBE versus carbon number for radical and protonated species for the O_2S_2 class from the PTFE subfractions. The results demonstrate that radical cations tend to occupy a high-DBE compositional range, with higher abundance-weighted DBE values and lower abundance-weighted H/C ratios than the protonated species. For both types of cations, the H/C ratio increases as a function of the extraction period. Figure 8, lower panel, presents bar graphs for the abundance-weighted H/C ratios (left) and the ratio of the relative abundance of protonated molecules to radical cations (right, $[M + H]^+/M^{+\bullet}$). It is clear that the residue is enriched in O_2S_2 species that preferentially ionize via protonation and occupy a compositional range shifted toward lower DBE values and higher H/C ratios. Several authors have suggested a direct correlation between proton affinities in the

gas phase and the tendency to hydrogen bond in solution.^{97–99} Moreover, it is well known that sulfoxides [R-S(=O)-R'] are weak bases that produce protonated molecules in electrospray ionization.¹⁰⁰ These results suggest that the most insoluble subfractions are enriched in low-DBE S-containing compounds (likely sulfoxides) with higher gas-phase proton affinities, which correlates with their ability to hydrogen bond in solution.

Supporting Information, Figures S4 and S5, presents separate isoabundance color-contoured plots of DBE versus carbon number for radical cations and protonated molecules for the O_1S_2 and O_3S_2 classes. Bar graphs for abundanceweighted H/C ratios (bottom left) and the ratio of the relative abundance of protonated molecules to radical cations (bottom right, $[M + H]^+/M^{+\bullet}$ are also included. The compositional trends are similar to the O₂S₂ class. Radical cations have higher DBE values than protonated species. Also, three-months and residue subfractions are enriched in low-DBE compounds with higher H/C ratios that produce abundant protonated molecules by APPI. It is important to note the clear correlation between oxygen content and gas-phase proton affinity. For instance, the residue $[M + H]^+/M^{+\bullet}$ ratios for the classes O_1S_2 , O_2S_2 , and O_3S_2 , are ~0.8, ~1.3, and ~3.4. Similarly, threemonth subfraction $[M + H]^+/M^{+\bullet}$ ratios are ~1.0, ~1.5, and ~1.6.

Low-DBE Asphaltene Species are Interfacially Active. Interfacially active asphaltenes were isolated from the whole Wyoming acetone fraction by the use of the wet silica method,^{67,80} with slight modifications. It is well known that asphaltenes exhibit strong, and in some cases, irreversible adsorption on chromatographic stationary phases.^{101–104} The mixture of THF/Tol/MeOH, used for the elution of interfacially active compounds, helps to decrease the amount of irreversibly adsorbed material on the silica gel. Figure 9 presents the isoabundance color-contoured plots of DBE versus carbon number for the O_1S_2 , O_2S_2 , and O_3S_2 classes, for



Figure 9. Upper panel: Isoabundance color-contoured plots of DBE vs carbon number for radical cations $M^{+\bullet}$ (left) and protonated molecules $[M + H]^+$ (right) for $O_x S_2$ species for the interfacial material isolated extracted from the Wyoming acetone fraction. Lower panel: $[M + H]^+/M^{+\bullet}$ abundance ratio. The results demonstrate similarity between the molecular composition of low-DBE asphaltenes and interfacially active species.

the interfacially active subfraction from the Wyoming acetone fraction. Radical cations and protonated molecules are plotted

separately. Note that the low-DBE O_2S_2 and O_3S_2 species in the PTFE residue (Figures 8 and S5) overlap the compositional range of the interfacially active subfraction (Figure 9).

Figure 9 also includes the abundance-weighted DBE and H/ C ratios, and the ratio of the relative abundance of protonated molecules to radical cations $([M + H]^+/M^{+\bullet})$. The preferential production of protonated species from the interfacial material supports the hypothetical central role of hydrogen bonding in the solubility behavior of low-DBE asphaltenes. The relative abundance of protonated species, for the classes O_1S_2 , O_2S_2 , and O_3S_2 , is ~11-, ~4-, and ~20-fold higher than the abundance of radical cations. It is well known that hydrogen bonds between interfacially active petroleum compounds and water are pivotal in emulsion stabilization.¹⁰⁵⁻¹⁰⁹ Therefore, the similarity between the composition of the interfacial material and the PTFE residue points to hydrogen bonding as an important interaction in asphaltene behavior. We hypothesize that interfacially active low-DBE compounds report as asphaltenes because their functional groups can hydrogen-bond with several neighboring molecules. For Wyoming deposit nC_7 asphaltenes, such species concentrate in the most insoluble PTFE subfractions.

Several studies support the existence of low-DBE, polyfunctional asphaltene species with pronounced interfacial activity. Kilpatrick pointed out that polarizable asphaltene fractions with poor solubility in toluene and stronger aggregation trends in Hep/Tol disproportionately contribute to emulsion stability.¹¹⁰ The author suggested that interfacially active asphaltene species are likely polyfunctional and capable of interacting with neighboring asphaltene molecules via several intermolecular forces of different natures, for example, π stacking, London forces between hydrophobic moieties, and hydrogen bonding. Among all these forces, hydrogen bonds could be of highest importance because of their longer lifetimes.^{46,110} Moreover, several authors have acknowledged the existence of polyfunctional asphaltene compounds with stronger aggregation trends and emulsion stabilization proper-



Figure 10. Top: Fragmentation mass spectra. Bottom: Isoabundance color-contoured plots of DBE vs carbon number for HCs, monoheteroatomic (i.e., N_1 , O_1 , and S_1), and polyheteroatomic classes (e.g., N_1O_1 , O_2 , and O_1S_1) for the precursor and fragment ions for one-day (left) and residue (right) PTFE subfractions. The results suggest that the residue is enriched in archipelago species with more extensive fragmentation by IRMPD.

ties.^{111–113} Recent reports by Czarnecki and Stanford suggest that interfacially active asphaltene species exhibit low-DBE values and multiple oxygen-containing functionalities likely capable of interacting with neighboring molecules through several hydrogen bonds.^{114–116}

Structural Characterization by Infrared Multiphoton Dissociation. To assess the general structure of the samples (island vs archipelago), high-DBE precursor ions (DBE > 20) for the one-day and residue subfractions were isolated at m/z602-605 and fragmented by IRMPD. The dissociation trends of high-DBE precursor ions enable determination of the changes in DBE after IRMPD, which is the basis to differentiate between island and archipelago structures.⁷¹ In tandem MS, island motifs lose only carbon number, whereas archipelago structures lose both carbon number and DBE. Moreover, this work focuses on the dissociation of high m/zions because the ratio, archipelago/island, is nonuniform throughout the molecular weight distribution, and increases as a function of increasing molecular weight.53,54 Therefore, samples that contain high-m/z ions (m/z > 550) with predominant fragmentation routes consistent with island structures are likely enriched in those motifs throughout the molecular weight distribution.53,54,117

Figure 10 shows the fragmentation spectra and the isoabundance color-contoured plots of DBE versus carbon number for precursor ions and fragments for the one-day subfraction (left) and the residue (right). The one-day subfraction is enriched in stable compounds unsuited for structural dissociation. The fragment ions comprise only $\sim 10\%$ of the mass spectrum and the DBE versus carbon number plots indicate that island structures are dominant. Most of the HC (HC class, ~52%), monoheteroatomic (i.e., N_1 , O_1 , and S_1 , classes, \sim 75%), and polyheteroatomic fragments (e.g., O₃, N_1O_{22} and O_3S_{22} ~95%) exhibit the same range of DBE values as the precursor ions. On the contrary, the residue presents a more "reactive" behavior; the fragments comprise ~47% of the fragmentation spectrum. The DBE versus carbon number plots suggest that the residue is enriched in archipelago species. Most of the HCs (96%) and monoheteroatomic (69%) fragments exhibit DBE values between 4 and 20, considerably lower than those of the precursor ions. The polyheteroatomic species do not show extensive change of DBE after dissociation. Here, it is important to note that the lack of abundant detection of low-DBE, polyheteroatomic fragments is not necessarily evidence for the dominance of island motifs. Indeed, polyheteroatomic compounds that contain heteroatoms in separate, alkyl-bridged aromatic cores will produce monoheteroatomic and/or HC species after dissociation. Also, the increased reactivity of the residue in IRMPD could arise from the higher content of oxygen-containing functionalities (e.g., carboxylic acid, ketone, and sulfoxide), which are known for their efficient absorption of infrared light.

Collectively, the results suggest that the most insoluble asphaltene subfraction, the residue, is enriched in oxygencontaining polyfunctional species that occupy a diverse compositional range, revealing high-DBE/alkyl-deficient asphaltenes and low-DBE/alkyl-enriched compounds. The fragmentation behavior of high-DBE HC and monoheteroatomic precursor ions demonstrates enrichment in archipelago motifs.

Differential Precipitation Applied to the Fractionation of Athabasca Bitumen Asphaltenes. Differential precipitation offers a second approach to understand the compositional trends responsible for asphaltene solubility. We hypothesize that the fractionation of Wyoming deposit asphaltenes by extended extraction with heptane may be dominated by aggregation-disaggregation kinetics, in which solubility may also play a role. On the other hand, the separation of Athabasca bitumen asphaltenes by differential precipitation is based on solubility, in which both structures of individual molecules and aggregated species are involved. Moreover, differential precipitation, also based on partitioning in *n*-heptane, does not involve the use of a stationary phase and extended periods of extraction processes that occur at liquid/ solid interfaces; therefore, possible oxidation is minimized.

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The acetone fraction from Athabasca bitumen asphaltenes is enriched in archipelago motifs and occupies a compositional range at lower DBE values (DBE \sim 3–30) and more extended homologous series.⁵⁴ Moreover, the Athabasca bitumen acetone fraction reveals abundant vanadyl porphyrins by positive-ion APPI, relative to the rest of the extrography fractions (e.g., Tol/THF and THF/MeOH).⁵⁴ Figure 11,



Figure 11. Upper panel: Fractionation of the Athabasca bitumen acetone fraction differential precipitation in Hep/Tol. Lower panel: Mass yield for the fractionation process and MIY from positive-ion APPI MS analyses. The results confirm that asphaltene aggregation restricts the production of ions in atmospheric pressure photo-ionization.

upper panel, illustrates the fractionation by differential precipitation. The separation of asphaltenes into fractions with discrete composition is challenging because of asphaltene extreme polydispersity. It is well known that ultrasound-assisted precipitation and crystallization processes yield aggregates and crystals with decreased content of impurities.^{118,119} In asphaltene precipitation, it is likely that sonication improves the incorporation of *n*-heptane into the asphaltene dispersions, providing a more selective precipitation process that yields asphaltene subfractions with pronounced differences in composition.

In differential precipitation, the first precipitated fractions (40 and 60% v/v Hep/Tol) are the least soluble in heptane and are the most polarizable species. As the fractionation process progresses, the supernatant enriches in *n*-heptane and more soluble asphaltene species. Figure 11, lower panel, presents the mass yield for the fractionation process (gray bars). Although the fractionation processes employed are

different (differential precipitation vs sequential extraction from PTFE by *n*-heptane), the results suggest that Athabasca bitumen asphaltenes exhibit a lower degree of partitioning in *n*heptane than Wyoming deposit asphaltenes. Approximately 70 wt % of the sample is recovered in the first two precipitation cycles, accounting for a considerable concentration of more polarizable/insoluble species. With regard to the ionization efficiency by positive-ion APPI (MIY, red bars), Athabasca bitumen acetone subfractions exhibit the same trends as Wyoming acetone species in the PTFE extractions (Figure 1). The results confirm a direct correlation between ion production by APPI and asphaltene partitioning in *n*C₇. An increased solubility in *n*-heptane (low degree of selfassociation) results in species that exhibit a high MIY (high ionization efficiency).

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Compositional Trends for the Solubility Fractions from Athabasca Bitumen Asphaltenes. Figure 12, upper



Figure 12. Heteroatom group distributions for the differential precipitation subfractions from the Athabasca bitumen acetone fraction. The results indicate that the species with the highest partitioning in *n*-heptane are enriched in HC, sulfur (S_x) , and nitrogen-containing compounds (N_x) , whereas the least soluble fractions are enriched in oxygen-containing species.

panel, shows the heteroatom group distribution for the differential precipitation subfractions from the Athabasca bitumen acetone fraction. The most insoluble subfraction (PPT/40, green bars) is enriched in oxygen-containing compounds; O_x and N_xO_y species have relative abundance ~3- and ~2-fold higher than the most soluble subfraction (Soluble/95, orange bars). On the other hand, the Soluble/95 subfraction is enriched in HCs, sulfur- and nitrogen-containing species (HC, S_{xy} N_xS_y , and N_x). Figure 12, lower panel, illustrates the progression of the oxygen continuum for the O_x group as a function of increasing nC_7 solubility. The results agree with the compositional trends for Wyoming deposit asphaltenes; the most insoluble subfraction is enriched in polyoxygenated species (O_2 , O_3 , O_4 , and O_5). For instance, PPT/

40 exhibits classes O_3 and O_4 with a ~7- and ~17-fold higher relative abundance than the Soluble/95 subfraction. The results support the existence of poly-functional oxygen-containing asphaltenes and their central role in stronger intermolecular interactions between asphaltenes.

Figure 13 presents the isoabundance color-contoured plots of DBE versus carbon number for the HC, S₁, and N₁ classes for the differential precipitation subfractions from the Athabasca bitumen acetone fraction. Radical cations and protonated molecules are plotted together. The most insoluble subfractions (PPT/40 and PP/T60) exhibit higher-abundance HC and S_1 low-DBE species (<10), whereas the most soluble compounds tend to occupy a more aromatic compositional range. In general, the abundance-weighted DBE values for the classes HC, S₁, and N₁ increase as a function of increasing nheptane solubility. However, the most soluble subfraction (Soluble/95) exhibits longer homologous series that extend to carbon numbers beyond \sim 55, whereas the homologous series of the most insoluble subfractions are limited to no more than ~40 carbon atoms. Therefore, the behavior of Athabasca bitumen subfractions suggests that asphaltene partitioning/ solubility in Hep/Tol is a complex phenomenon governed by a delicate balance between the aromatic core size (DBE) and alkyl substitution.49,120

Supporting Information, Figures S6 and S7, show the compositional range for the classes S_1 , S_2 , S_3 , and N_1O_x . The results indicate that the most insoluble subfractions (PPT/40 and PPT/60) are enriched in alkyl-deficient compounds with DBE values between 7 and 15. Such DBE values suggest the presence of small aromatic cores consisting of 2–5 fused-rings, quite small compared to the proposed asphaltene model compounds and structures detected by atomic force microscopy.^{12,13,16,18} Figure S8 of the Supporting Information suggests that alkyl-substitution increases solubility of vanadyl porphyrins in nC_7 .

Athabasca Bitumen Asphaltenes Also Exhibit Low-**DBE** $O_x S_v$ Species. Figure 14, upper panel, presents separate DBE versus carbon number plots for radical cations M^{+•} and protonated species $[M + H]^+$ for the O_1S_2 class for the Athabasca bitumen subfractions. The lower panel includes bar graphs for the abundance-weighted H/C ratios and the ratio of the relative abundance of protonated molecules to radical cations $([M + H]^+/M^{+\bullet})$. The compositional trends are similar to those observed for the Wyoming deposit. First, the protonated species occupy a compositional range different from that for radical cations. Second, the most insoluble compounds exhibit lower abundance-weighted DBE; and third, the most insoluble subfractions (PPT/40 and PPT/60) preferentially produce protonated molecules by APPI, suggesting higher proton affinities in the gas phase and hydrogen bonding interactions in solution.

It is important to note that the effect of alkyl substitution on the solubility of heteroatomic compounds for Athabasca bitumen subfractions appears opposite to that for the Wyoming PTFE species. The higher content of CH_2 units produces steric hindrance around the active sites responsible for intermolecular interactions, increasing asphaltene solubility in Hep/Tol. Thus, the species that comprise the Soluble/95 subfraction exhibit the highest DBE values, but are more soluble in Hep/Tol because of their greater content of CH_2 units. Figures S9 and S10 of the Supporting Information indicate that the O_2S_2 and O_2S_1 classes present compositional trends similar to those for the O_1S_2 species.

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Figure 13. Isoabundance color-contoured plots of DBE vs carbon number for the HC, S_1 , and N_1 classes for the differential precipitation subfractions from Athabasca bitumen. Radical cations (M^{++}) and protonated molecules ($[M + H]^+$) are plotted together. The results suggest that asphaltene solubility in Hep/Tol is governed by a delicate balance between the aromatic core size and alkyl chain content.



Figure 14. Upper panel: Separate isoabundance color-contoured plots of DBE vs carbon number for radical cations $M^{+\bullet}$ and protonated species $[M + H]^+$ for the O_1S_2 class for the differential precipitation subfractions from Athabasca bitumen. Lower panel: Abundance-weighted H/C ratio and ratio of the relative abundance of protonated molecules to radical cations ($[M + H]^+/M^{+\bullet}$). The results support the existence of low-DBE/highly insoluble asphaltenes that preferentially yield protonated cations in atmospheric pressure photoionization.

Finally, Figure S11 of the Supporting Information presents the fragmentation spectra for high-DBE precursor ions isolated at m/z 650–655, for both the most insoluble (left) and soluble (right) subfractions from Athabasca bitumen acetone asphaltenes (PPT/40 and Soluble/95). In the third part of the series "Advances in Asphaltene Petroleomics", it was demonstrated that the acetone extrography fraction from Athabasca bitumen asphaltenes is enriched in archipelago motifs.⁵⁴ Figure S11 demonstrates that regardless of solubility, Athabasca bitumen species reveal dominant archipelago structures. Moreover, the dissociation trends agree with the fragmentation behavior of Wyoming deposit asphaltenes. The most insoluble species (PPT/40) yield abundant fragments by IRMPD: the fragments comprise \sim 65% of the fragmentation spectrum relative to the precursor ions, compared to the most soluble compounds (only \sim 27%).

CONCLUSIONS

Two asphaltene extrography fractions, enriched in *island* (Wyoming acetone) or *archipelago* motifs (Athabasca bitumen acetone), were separated into solubility cuts by extended extraction with *n*-heptane and differential precipitation in

Hep/Tol. The ionization efficiency trends for the solubility subfractions suggest that asphaltene aggregation precludes the complete characterization of the unfractionated sample by mass spectrometry. The most soluble subfractions exhibit up to \sim 30-fold higher MIY than the least soluble species.

The compositional trends, accessed by + APPI 9.4 T FT-ICR MS, suggest that HCs, sulfur (S_x) , and nitrogencontaining (N_xS_y, N_x) compounds do not promote stronger intermolecular interactions because their relative abundances decrease as a function of the decreasing partition in nC_7 . In the case of a sample, in part, consistent with the modified Yen model, such as the Wyoming acetone fraction, the behavior of HC species with no heteroatoms supports that both DBE and hydrogen deficiency increase as a function of *n*-heptane insolubility.

On the other hand, the progression of the compositional range of oxygen-containing species points to the Boduszynski continuum as a possible basis for a new asphaltene aggregation model. Higher-order oxygen-containing compounds contain lower abundance-weighted DBE values, suggesting that lower aromaticity is offset by higher oxygen content. Moreover, for both Wyoming and Athabasca bitumen, the compositional trends indicate that the most insoluble subfractions are enriched in polyoxygenated compounds. In particular, sulfurcontaining polyoxygenated classes $(O_2S_2 \text{ and } O_3S_2)$, with low DBE values (<10) concentrate in the most insoluble subfractions and yield abundant protonated molecules by atmospheric pressure photoionization. The similarity between the composition of low-DBE $O_x S_y$ species and the interfacial material extracted from the parent acetone fractions supports the central role of hydrogen bonding in the solubility/ aggregation behavior of petroleum asphaltenes. It is very likely that low-DBE species, with high oxygen content and low DBE values, reside in the most insoluble asphaltene subfractions because of extensive hydrogen bonding with several neighboring molecules.

Collectively, the results highlight the need for an aggregation model that acknowledges the coexistence of (1) monofunctional and polyfunctional species; (2) island and archipelago motifs; and (3) high- and low-DBE asphaltene compounds. The strong aggregation of such a complex mixture must be the result of the synergy between π -stacking, London forces, hydrogen bonds, and acid/base interactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.9b04288.

Figure captions (PDF)

DBE versus carbon number plots for S_x species for PTFE subfractions from the Wyoming acetone fraction. Radical cations and protonated molecules are plotted together (PDF)

DBE versus carbon number plots for N_x species for PTFE subfractions from the Wyoming acetone fraction. Radical cations and protonated molecules are plotted together (PDF)

DBE versus carbon number plots for N_1O_x species for PTFE subfractions from the Wyoming acetone fraction. Radical cations and protonated molecules are plotted together (PDF) Separate DBE versus carbon number plots for radical and protonated O_1S_2 species for PTFE subfractions from the Wyoming acetone fraction, and bar graphs for the abundance-weighted H/C ratios and ratio of the relative abundance of protonated molecules to radical cations (PDF)

Separate DBE versus carbon number plots for radical and protonated O_3S_2 species for PTFE subfractions from the Wyoming acetone fraction, and bar graphs for the abundance-weighted H/C ratios and ratio of the relative abundance of protonated molecules to radical cations (PDF)

DBE versus carbon number plots for S_x species for differential precipitation subfractions from the Athabasca bitumen acetone fraction. Radical cations and protonated molecules are plotted together (PDF)

DBE versus carbon number plots for N_1O_x species for differential precipitation subfractions from the Athabasca bitumen acetone fraction. Radical cations and protonated molecules are plotted together (PDF)

DBE versus carbon number plots for $N_4O_1V_1$ species for differential precipitation subfractions from the Athabasca bitumen acetone fraction. Radical cations and protonated molecules are plotted together (PDF)

Separate DBE versus carbon number plots for radical and protonated O_1S_2 species for differential precipitation subfractions from the Athabasca bitumen acetone fraction, and bar graphs for the abundance-weighted H/C ratios and ratio of the relative abundance of protonated molecules to radical cations (PDF)

Separate DBE versus carbon number plots for radical and protonated O_2S_2 species for differential precipitation subfractions from the Athabasca bitumen acetone fraction, and bar graphs for the abundance-weighted H/C ratios and ratio of the relative abundance of protonated molecules to radical cations (PDF)

Fragmentation behavior for differential precipitation subfractions from Athabasca bitumen C_7 asphaltenes: PPT/40 and Soluble/95 (PDF)

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Notes

The authors declare no competing financial interest.

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